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W-8000 München 81(DE)**(54) **METHOD AND DEVICE FOR COATING.**

(57) The invention relates to metallurgy. The proposed method for coating of articles provides for introducing into a gas flow the powder of a material chosen from a group consisting of metals, alloys and their mechanical mixtures, or dielectrics, and having a particle size of 1 to about 50  $\mu\text{m}$ , in a quantity sufficient to ensure a mass flux density of the particles of 0.05 to 17 g/sec.cm<sup>2</sup>, so as to form a gas-powder mixture which is directed on the surface of the article, the gas flow being given a supersonic speed and being formed into a supersonic jet of a desired profile providing for a speed of the powder particles in the gas-powder mixture of 300-1,200 m/sec. A device for implementation of the method comprises a doser-feeder (1) and, interconnected to each other, a bunker (2) for the powder, a means for dosing it consisting of a horizontally mounted drum (9) with recesses provided along a spiral line on its cylindrical surface (9'), a mixing chamber (3), a nozzle (4) intended for acceleration of the powder particles and connected to the mixing chamber (3), a compressed air source (5) connected to a means for feeding the compressed air to the mixing chamber (3), a flow regulator (11) for the powder articles mounted in relation to the cylindrical surface (9') of the drum (9) with a gap (12) ensuring the required mass flow of the powder, and intermediate nozzle (13) coupled with the mixing chamber (3) and

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connecting through its inlet pipe (8) to the means for feeding the compressed air, and a baffle (15) mounted on the bottom of the bunker (2) and in close proximity to the cylindrical surface (9') of the drum, the nozzle (4) for acceleration of the powder particles having a supersonic design and being provided with a profiled channel (18).

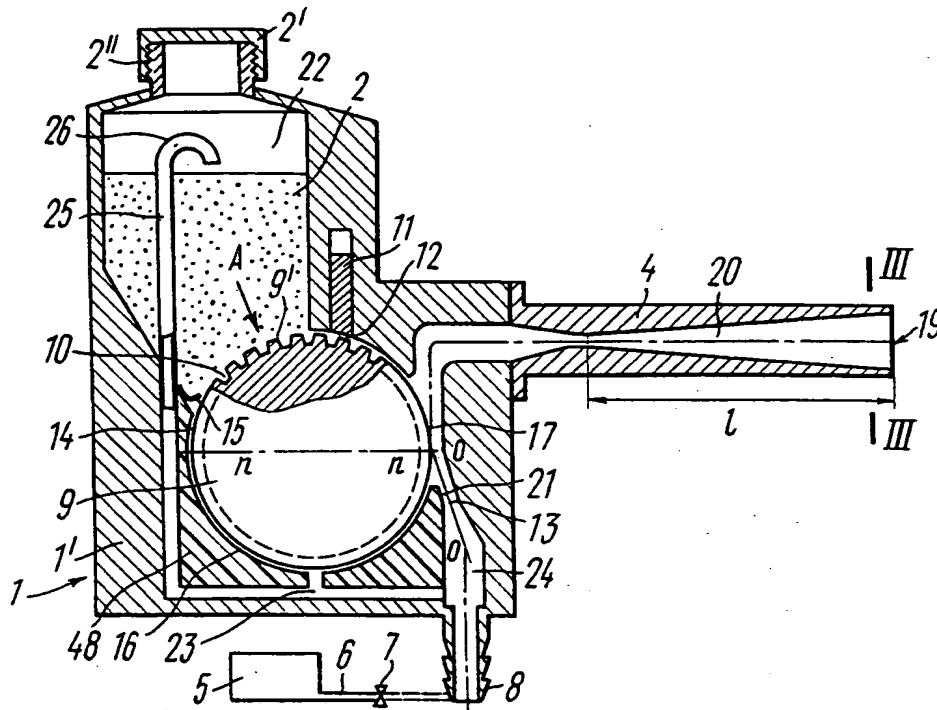


FIG. 1

## Technical Field

The invention relates to the metallurgy, and more specifically, it deals with method and apparatus for applying a coating.

## Background Art

Protection of structures, equipment, machines, and mechanisms made of ferrous metals against corrosion and action by aggressive media, enhancement of technical characteristics of materials, including the preparation of materials with expected properties, and development of resource-saving manufacturing processes is an important scientific, technological and practical problems.

These problems can be solved by using various methods, including deposition of powder coatings and, among others, with the use of most popular gas flame-spray, electric arc, explosive, and plasma methods.

The gas flame-spray method is based on the use of gas combustion products at 1000 to 3000 °C, and creation of a flow of such gases in which particles of the powder being applied are fused. A velocity of 50 to 100 m/s is imparted to particles of the powder, and the surface is treated with the gas and powder flow containing the fused particles. This treatment results in a coating being formed. Low values of velocity and temperature of the applied particles substantially limit application of this method.

The explosive method is partly free of these disadvantages. With this method, energy of detonating gases at 2000 to 3500 °C is used so as to substantially increase the velocity of the particles up to 400 to 700 m/s and their temperature, up to 2000 to 3500 °C to ensure application of coatings with powders of metals, alloys, and insulating materials. This method is very disadvantageous in a low productivity because of the pulsed character of deposition: the resulting shock wave and a gas flow accompanying it cause a high level of a thermal and dynamic action upon the product and high level of acoustic noise which restricts application of this method.

The most promising is a method of plasma deposition wherein a powder coating is applied to a product surface with a high-temperature gas jet (5000 to 30000 °C).

Known in the art is a method for applying coatings to the surface of a product made of a material selected from the group consisting of metals, alloys, and insulating materials, comprising introducing into a gas flow a powder of a material selected from the group consisting of metals, alloys, their mechanical mixtures or insulating materials for forming a gas and powder mixture which is directed towards the surface of a product (in the book by V.V. Kudinov, V.M. Ivanov. Nanesenie Plazmoi Tugoplavkikh Pokryty /Application of Refractory Coatings with Plasma/. Mashinostroenie Publishing House, Moscow. 1981, pp. 9 to 14).

The prior art method is characterized in that powder particles of a size from 40 to 100 μm are introduced into a high-temperature gas flow (5000 to 30000 °C) in the form of a plasma jet. Powder particles are heated to the melting point or above that point, accelerated with the gas flow of the plasma jet and directed at the surface being coated. Upon impingement, particles of the powder interact with the surface of the product so as to form a coating. In the prior art method, powder particles are accelerated by the high-temperature plasma jet and are transferred, in the molten state, to the product being coated; as a result, the high-temperature jet runs into the product to exert a thermal and dynamic action upon its surface, i.e., to cause local heating, oxidation and thermal deformations. Thus, thin-walled products are heated up to 550 °C, they are oxidized and warped, and the coating peels off.

The high-temperature jet running into the product surface intensifies chemical and thermal processes, causes phase transformations and appearance of over-saturated and non-stoichiometric structures, hence, results in the material structure being changed. In addition, a high level of thermal exposure of the coating results in hardening of heated melts and gas release during solidification which causes formation of a large porosity and appearance of microcracks, i.e., impairs technical characteristics of the coating.

It is known that, with an increase in temperature of plasma jet, plasma density in comparison with gas density under normal conditions linearly decreases, i.e., at 10000 °C, density of the jet becomes scores of times lower which results in a respective decrease in the coefficient of drag. As a result, with an escape velocity of the plasma jet of 1000 to 2000 m/s (which is about equal to, or slightly below then, the sonic velocity), the particles are accelerated up to 50 to 200 m/s (even up to 350 m/s at best), i.e., the process of acceleration is not efficient enough.

Heating, melting, and overheating of particles of the powder in the plasma jet is known to be enhanced with a decrease in the particle size. As a result, fine fractions of powder of a size from 1 to 10  $\mu\text{m}$  are heated to a temperature above the melting point, and their material intensively evaporates. For this reason, plasma deposition of particles of a size below 20 to 40  $\mu\text{m}$  is very difficult, and particles of a size from 40 to 100  $\mu\text{m}$  are normally used for this purpose.

It should be also noted that the prior art method makes use of plasma jets of energy-consuming diatomic gases which call for application of high power resulting in stringent requirements being imposed upon structure of apparatuses. Limitations of application of the method for application of coatings to small-size objects are thus very strict and can only be eliminated by complete removal of the applied energy by means of cooling or by providing a dynamic vacuum, i.e., by evacuation of high-temperature gases which requires high power consumption.

Therefore, the prior art method has the following disadvantages: high level of thermal and dynamic exposure of the surface being coated; substantial changes in properties of the material being applied during the coating application, such as electrical conductance, heat conductance, and the like; changes in the structure of the material through phase transformations and appearance of oversaturated structures as a result of the chemical and thermal exposure to the plasma jet and hardening of overheated melts; ineffective acceleration of powder particles in view of a low density of plasma; intensive evaporation of fine powder fractions of a size from 1 to 10  $\mu\text{m}$ ; stringent requirements imposed upon structure of apparatuses in view of high-temperature processes of the prior art method.

Known in the art is an apparatus for carrying out the prior art method for applying coatings to the surface of a product, comprising a metering feeder having a casing incorporating a hopper for a powder communicating with a means for metering the powder in the form of a drum having depressions in its cylindrical periphery, and a mixing chamber communicating therewith, and a nozzle for accelerating powder particles communicating with the mixing chamber, a source of compressed gas, and a means connected thereto for supplying compressed gas to the mixing chamber (in the book by V.V.Kudinov, V.M. Ivanov, Nanesenie Plazmoi Tugoplavkikh Pokryty /Application of Refractory Coatings with Plasma/. Mashinostroenie Publishing House, Moscow. 1981, pp. 20 to 21, Fig. 11; p. 26, Fig. 13).

The prior art apparatus is characterized by having a plasma sprayer (plasmotron), comprising a cylindrical (subsonic) nozzle having passages for supplying plasma-forming gas and water for cooling thermally stressed components of the plasma sprayer (namely, of the nozzle) in which refractory materials are used. Powder particles are introduced from the metering feeder at the edge of the nozzle.

Since energy for forming plasma jet is applied in the form of an arc in the passage of the plasmotron nozzle, the nozzle is subjected to an intensive electric erosion and high-temperature exposure. As a result, a rapid erosion wear of the nozzle occurs, and service life of the nozzle is 15 to 20 hours. With a complicated structure and use of refractory materials and water cooling service life can be prolonged to 100 hours.

The introduction of the particles at the edge of the nozzle and erosion of the inner duct of the nozzle lower efficiency of acceleration of the powder particles. Thus, in combination with a low density of plasma, the prior art apparatus ensures a velocity of powder particles of up to 300 m/s with a gas escape velocity of up to 1000 m/s.

As a result of the powder getting into the space between moving parts of the metering feeder (e.g., between the drum and casing), the drum can be jammed.

Therefore, the prior art apparatus has the following disadvantages: short service life which is mainly determined by service life of the nozzle of 15 to 100 hours and which is associated with high density of thermal flux in the direction towards the plasmotron nozzle and erosion of the electrodes so that expensive, refractory, and erosion-resistant materials should be used; inefficient acceleration of the deposited particles because the nozzle shape is not optimum and is subjected to changes as a result of electrical erosion of the inner duct; unreliable operation of the metering feeder of the drum type which is caused by the powder getting into the space between the moving parts to result in their jamming.

#### Disclosure of the Invention

The invention is based on the problem of providing a method and apparatus for applying a coating to the surface of a product which allow the level of thermal and dynamic and thermal and chemical action upon the surface being coated and upon powder particles to be substantially lowered and initial structure of the powder material to be substantially preserved, without phase transformations, appearance of oversaturated structures, and hardening during application and formation of coatings, efficiency of acceleration of powder particles being applied to be enhanced, evaporation of fine fractions of the powder with a particle

size from 1 to 10  $\mu\text{m}$  to be eliminated, lower level of thermal and erosion exposure of components of the apparatus to be ensured, with a service life of the apparatus being prolonged up to 1000 hours without the use of expensive, refractory, and erosion-resistant materials, with an improvement of operation of the duct in which powder particles are accelerated and with enhanced reliability of the metering feeder in operation even in metering fine powder fractions.

The problem set forth is accomplished by providing a method for applying a coating to the surface of a product made of a material selected from the group consisting of metals, alloys, and insulating materials, comprising introducing into a gas flow a powder of a material selected from the group consisting of metals, alloys, their mechanical mixtures or insulating materials for forming a gas and powder mixture which is directed towards the surface of a product, wherein, according to the invention, the powder used has a particle size from 1 to 50  $\mu\text{m}$  in an amount ensuring flow rate density of the particles between about 0.05 and about 17 g/s  $\text{cm}^2$ , a supersonic velocity being imparted to the gas flow, and a supersonic jet of a predetermined profile being formed which ensures a velocity of powder in the gas and powder mixture from 300 to 1200 m/s.

Owing to the fact that the powder is used with a particle size from 1 to 50  $\mu\text{m}$ , denser coatings can be produced, filling of the coating layer and its continuity are improved, the volume of microvoids decreases, and structure of the coating becomes more uniform, i.e., its corrosion resistance, hardness, and strength are enhanced.

A density of flow rate of the particles between about 0.05 and about 17 g/s  $\text{cm}^2$  increases the degree of utilization of the particles, hence, productivity of coating application. With a flow rate of particles below 0.05 g/s  $\text{cm}^2$ , the degree of utilization is close to zero, and with the degree of utilization above 17 g/s  $\text{cm}^2$ , the process becomes economically ineffective.

The formation of the supersonic jet ensures acceleration of the powder in the gas stream and lowers temperature of the gas flow owing to gas expansion upon its supersonic escape. The formation of the supersonic jet of a predetermined profile with a high density and at low temperature, owing to an increase in the coefficient of drag of the particles with an increase in gas density and a decrease in temperature, ensures a more efficient acceleration of powder particles and a decrease in thickness of the compressed gas layer in front of the product being coated, hence, a lower decrease in velocity of the particles in the compressed gas layer, a decrease in the level of thermal and dynamic and thermal and chemical exposure of the surface being coated and particles of the powder being applied, elimination of evaporation of particles of a size from 1 to 10  $\mu\text{m}$ , preservation of the initial structure of the powder material and elimination of hardening of the coating and thermal erosion of components of the apparatus.

Imparting an acceleration to the gas and powder mixture to a velocity of from 300 to 1200 m/s ensures high level of kinetic energy of the powder particles which upon impingement of the particles against the surface of a product is transformed into plastic deformation of the particles and results in a bond being formed between them and the product.

Therefore, the invention, which makes use of finely-divided powder particles of a size from 1 to 50  $\mu\text{m}$  with a density of flow rate from 0.05 to 17 g/s  $\text{cm}^2$  and which contemplates imparting an acceleration to the powder particles by means of a supersonic jet of a predetermined profile and with a low gas temperature to a velocity of from 300 to 1200 m/s substantially lowers the level of thermal and dynamic and thermal and chemical exposure of the surface being coated and enhances efficiency of particles acceleration so as to ensure the production of denser coating microvoids, enhance the filling of the coating layer and its continuity. This results in a uniform structure of the coating with substantially preserved structure of the powder material without phase transformations and hardening, i.e., the coatings do not crack, their corrosion resistance, microhardness, and cohesion and adhesion strength are enhanced.

It is preferred that the supersonic jet of a predetermined profile be formed by carrying out gas expansion in accordance with a linear law. This facility ensures simplicity and low cost of manufacture of an apparatus for carrying out the method.

It is preferred that the gas flow be formed with a gas at a pressure of from about 5 to about 20 atm. and at a temperature below the melting point of the powder particles. As a result, efficient acceleration of powder particles is ensured because of a low density of the gas, thermal and dynamic and thermal and chemical exposure is lowered, and manufacture of an apparatus for carrying out the method is facilitated and its cost is reduced.

Air can be used as the gas for forming the gas flow. This ensures the acceleration of the powder particles to a velocity of up to 300 to 600 m/s and allows savings to be achieved during coating application.

It is preferred that helium be used as the gas for forming the gas flow. This facility allows a velocity of from 1000 to 1200 m/s to be imparted to the powder particles.

It is preferred that the a mixture of air and helium be used as the gas for forming the gas flow. The mixture of air and helium allows the velocity of the powder particles to be controlled within the range from 300 to 1200 m/s.

Particle velocity can also be controlled between 300 and 1200 m/s by heating the gas to from 30 to 400 °C, which is advantageous from the manufacturing and economic points of view so as to lower the cost of coating application because air can be used in this case, and the velocity of the powder particles can be controlled over a wide range.

The above problem is also solved by providing an apparatus for carrying out the method for applying a coating to the surface of a product, comprising a metering feeder having a casing incorporating a hopper for a powder communicating with a means for metering the powder in the form of a drum having depressions in its cylindrical periphery, and a mixing chamber communicating therewith, and a nozzle for accelerating powder particles communicating with the mixing chamber, a source of compressed gas, and a means connected thereto for supplying compressed gas to the mixing chamber, which, according to the invention, comprises a powder particle flow controller which is mounted in a spaced relation to the cylindrical periphery of the drum, with a space ensuring the necessary flow rate of the powder, and an intermediate nozzle coupled to the mixing chamber and communicating, via an inlet pipe thereof, with the means for supplying compressed gas, the metering feeder having a deflector mounted on the bottom of the hopper adjacent to the cylindrical periphery of the drum which has its depressions extending along a helical line, the drum being mounted horizontally in such a manner that one portion of its cylindrical periphery defines the bottom of the hopper and the other part thereof defines the generant of the mixing chamber, the particle acceleration nozzle being in the form of a supersonic nozzle and having a profiled passage.

The provision of the powder particle flow controller ensures the desired flow rate of the powder during coating application.

The provision of the deflector mounted on the hopper bottom prevents powder particles from getting into the space between the drum and the casing of the metering feeder so as to avoid jamming of the drum.

The provision of the depressions on the cylindrical periphery of the drum extending along a helical line lower fluctuations of the flow rate of the particles during metering.

The provision of a portion of the drum functioning as the hopper bottom and of the other portion of the drum functioning as the generant of the mixing chamber ensures uniform filling of the depressions with the powder and reliable admission of the powder to the mixing chamber.

The provision of the supersonic nozzle having a profiled passage allows a supersonic velocity to be imparted to the gas flow and a supersonic jet of a predetermined profile to be formed with high density and low temperature so as to ensure acceleration of the powder particles of a size from 1 to 50  $\mu\text{m}$  to a velocity from 300 to 1200 m/s.

Since the mixing chamber and the intermediate nozzle connected thereto communicate with the means for supplying compressed gas through the inlet pipe of the intermediate nozzle, the metering feeder can be supplied from different compressed gas supplies, including portable and stationary gas supplies which can be installed at a substantial distance from the metering feeder.

It is preferred that the passage of the supersonic nozzle for acceleration of particles have one dimension of its cross-section larger than the other, with the ratio of the smaller dimension of the cross-section at the edge of the nozzle to the length of the supersonic portion of the passage ranging from about 0.04 to about 0.01.

This construction of the passage allows a gas and powder jet of a predetermined profile to be formed, ensures efficient acceleration of the powder, and lowers velocity decrease in the compressed gas layer in front of the surface being coated.

A swirl member for swirling the gas flow leaving the means for compressed gas supply may be provided on the inner surface of the intermediate nozzle, at the outlet thereof in the mixing chamber. This gas flow swirl member turbulizes the flow of gas directed from the cylindrical nozzle towards the cylindrical surface of the drum so as to ensure the effective removal of the powder and formation of the gas and powder mixture.

It is preferred that the intermediate nozzle be mounted in such a manner that its longitudinal axis extend at an angle from 80 to 85° with respect to a normal to the cylindrical surface of the drum. When the gas flow runs into the cylindrical surface of the drum, a recoil flow is formed so as to enhance efficiency of powder and gas mixing.

It is preferred that the apparatus comprise a means for supplying compressed gas to depressions in the cylindrical periphery of the drum and to the upper part of the hopper so as to even out pressure in the hopper and mixing chamber. This facility eliminates the effect of pressure on metering of the powder.

It is preferred that the means for gas supply be provided in the casing of the metering feeder in the form of a passage connecting the interior space of the intermediate nozzle to the interior space of the hopper and also comprise a tube connected to the intermediate nozzle and extending through the hopper, the top part of the tube being bent at 180°. This simplifies the design, enhances reliability in operation, and prevents the powder from getting into the passage during loading of the powder into the hopper.

It is preferred that the apparatus comprise a means for heating compressed gas having a gas temperature control system for controlling velocity of gas and powder mixture with the supersonic jet. This facility ensures gas escape velocity control by varying its temperature so that velocity of powder particles is also controlled.

To enhance heat transfer from the gas heater, the inlet of the means for gas heating may be connected, through a pneumatic line to the mixing chamber of the metering feeder and the outlet can be connected to the nozzle for acceleration of powder particles.

For applying coatings of polymeric materials, it is preferred that the apparatus comprise a forechamber for acceleration of powder particles, the inlets of the means for gas heating and of the inlet pipe of the intermediate nozzle of the metering feeder being connected, by means of individual pneumatic lines to a compressed gas supply and their outlets being connected to the forechamber by means of other individual pneumatic lines.

It is preferred that the heating means be provided with a heating element made of a resistor alloy. This allows the size of the heating means and its weight to be reduced.

To lower heat losses and enhance economic effectiveness of the apparatus, it is preferred that the heating element be mounted in a casing having a heat insulator inside thereof.

To make the heating means compact and to ensure heating with low temperature differentials between the gas and the heating element, the heating element may be made in the form of a spiral of a thin-walled tubes, with the gas flowing through the tube.

To ensure a substantial reduction of the effect of the gas supplied to the gas and powder mixture from the metering feeder on operation of the supersonic nozzle, it is preferred that the forechamber have a diaphragm mounted in its casing and having ports for evening out the gas flow over the cross-section and a pipe coaxially mounted in the diaphragm for introducing powder particles, the cross-sectional area of the pipe being substantially 5 to 15 times as small as the cross-sectional area of the pneumatic line connecting the gas heating means to the forechamber.

To lower wear of the drum, alterations of its surface, and reduce jamming, the drum may be mounted for rotation in a sleeve made of a plastic material which engages the cylindrical periphery of the drum.

The plastic material of the sleeve may be in the form of a fluoroplastic (teflon). This allows the shape of the drum to be retained owing to the absorption of the powder by the sleeve material.

#### Brief Description of the Drawings

The invention will now be described in detail with reference to specific embodiments illustrated in the accompanying drawings, in which:

Fig. 1 is a general view of an apparatus for applying a coating to the surface of a product according to the invention, a longitudinal section;

Fig. 2 is a detail in a view taken along arrow A in Fig. 1 showing location of depressions on the surface of a metering drum;

Fig. 3 is a cross-sectional view taken along line III-III in Fig. 1 showing a cross-section of the supersonic part of a nozzle;

Fig. 4 schematically shows an embodiment of an apparatus for applying a coating to the surface of a product having a gas heating means which is connected in series with the metering feeder according to the invention;

Fig. 5 is another embodiment of an apparatus according to the invention having a gas heating means connected in parallel with the metering feeder;

Fig. 6 is an enlarged view partially in section in Fig. 1.

#### Best Mode to Carry out the Invention

The invention contemplates a method for applying a coating to the surface of a product. The material of the product is selected from the group consisting of metals, alloys and insulating materials. In this case the materials may be in the form of a metal, ceramic or glass. The method consists in that a powder of a material selected from the group consisting of metals, alloys or their mechanical mixtures, and insulating

materials is introduced into a gas flow for forming a gas and powder mixture which is directed towards the surface of the product. According to the invention, powder has particles of a size from 1 to 50  $\mu\text{m}$  in an amount ensuring a density of flow rate of the particles between 0.05 and 17 g/s  $\text{cm}^2$ . A supersonic velocity is imparted to the gas flow, and a supersonic jet is formed with a predetermined profile and at a low temperature. The resulting gas and powder mixture is introduced into the supersonic jet to impart thereto an acceleration which ensures a velocity of the powder particles ranging from 300 to 1200 m/s.

If finely divided powder particles are used with the above-mentioned density of their flow rate, and if acceleration is imparted to the powder particles by means of a supersonic jet of a predetermined profile having high density and low gas temperature to a velocity ranging from 300 to 1200 m/s, a substantial decrease in the level of thermal and dynamic and thermal and chemical exposure of the surface being coated is ensured, and efficiency of acceleration of the powder particles is enhanced. This, in turn, results in denser coatings being produced, with a lower volume of microvoids and with enhanced continuity. The coating structure is uniform with the retention of substantially the initial structure of the powder material, without phase transformations, i.e., the coatings do not crack, their corrosion resistance, microhardness, cohesive and adhesive strength are enhanced.

In accordance with the invention, the gist of the method resides in the fact that coating application by spraying is effected by a high-velocity flow of powder which is in the solid state, i.e., at a temperature which is much lower than the melting point of the powder material. The coating is thus formed owing to the impact and kinetic energy of particles which is spent for high-speed plastic deformation of the interacting bodies in microvolumes which are commensurable with the particle size and also for local heat release and cohesion of particles with the surface being coated and with one another.

The formation of a supersonic jet of a predetermined profile is carried out by expanding gas according to a linear law so as to make the process simple and economical.

For forming a gas flow, a gas is used which is under a pressure of from about 5 to about 20 atm. and at a temperature below the melting point of the powder particles so as to ensure the efficient acceleration of the powder particles owing to a high density of the gas and to lower thermal and dynamic and thermal and chemical exposure.

Acceleration is imparted to the powder particles to a velocity ranging from about 300 to about 600 m/s by using air as gas for forming the gas flow.

To impart to the powder particles a velocity ranging from 1000 to 1200 m/s, helium is used, and to impart a velocity ranging from 300 to 1200 m/s a mixture of air and helium is used.

For accelerating various materials in the form of powder, gases are used which have different sound velocities at a constant temperature, which can impart different velocities to the powder particles. For such powders as tin, zinc, aluminium, and the like, use may be made of air, and air and helium mixture in various proportions may be used for nickel, iron, cobalt, and the like. By changing percentage of components, the velocity of escape of the gas jet, hence, the velocity of the powder particles, can be varied.

Another option for controlling the velocity of particles between 300 and 1200 m/s is the variation of the initial gas temperature. It is known that with an increase in gas temperature sound velocity in the gas increases. This allows the jet escape velocity, hence, velocity of the deposited powder particles to be controlled by a slight heating of the gas at 30 to 400 °C. During expansion of the gas, when the supersonic jet is formed, the gas temperature decreases substantially so as to maintain the thermal exposure of powder at a low level which is important in the application of polymeric coatings to products or their components.

An apparatus for applying coatings to the surface of a product comprises a metering feeder 1 (Fig. 1) having a casing 1' which accommodates a hopper 2 for powder having a lid 2' mounted by means of thread 2'', a means for metering powder, and a mixing chamber 3 communicating with one another. The apparatus also has a nozzle 4 for accelerating powder particles communicating with mixing chamber 3, a compressed gas supply 5, and a means connected thereto for supplying compressed gas to mixing chamber 3. The means for compressed gas supply is in the form of a pneumatic line 6 which connects, via a shut-off and control member 7, compressed gas supply 5 to an inlet pipe 8 of metering feeder 1. A means for metering powder is in the form of a cylindrical drum 9 having in its cylindrical periphery 9' depressions 10 and communicating with mixing chamber 3 and with particle accelerating nozzle 4.

According to the invention, the apparatus also comprises a powder particle flow controller 11 which is mounted in a spaced relation at 12 to cylindrical periphery 9' of drum 9 so as to ensure the desired flow rate of the powder during coating, and an intermediate nozzle 13 positioned adjacent to mixing chamber 3 and communicating, via inlet pipe 8, with the means for gas supply and with compressed gas supply 5.

To prevent powder particles from getting into a space 14 between drum 9 and casing 1' of metering feeder 1 so as to avoid jamming of drum 9, a deflector 15 is provided on the hopper bottom which intimately engages cylindrical periphery 9' of drum 9.

To ensure uniform filling of depressions 10 with powder and enhance its reliable admission to mixing chamber 3, drum 9 is mounted to extend horizontally in such a manner that one portion of its cylindrical periphery 9' is used as a bottom 16 of hopper 2 and the other portion forms a wall 17 of mixing chamber 3. Depressions 10 in cylindrical periphery 9' of drum 9 extend along a helical line (Fig. 2) so as to lower fluctuations of the flow rate of powder particles during metering. To impart to the gas flow a supersonic velocity with a predetermined profile, with high density and at low temperature, and also to ensure acceleration of powder particles to a velocity ranging from 300 to 1200 m/s, nozzle 4 for acceleration of particles is in the form of a supersonic nozzle and has a passage 18 of a profiled cross-section (Fig. 3). Passage 18 of nozzle 4 has one dimension "a" of its cross-section which is larger than the other dimension "b", and the ratio of the smaller dimension "b" of the cross-section at an edge 19 of nozzle 4 (Fig. 1) to length "l" of a supersonic portion 20 of passage 18 ranges from about 0.04 to about 0.01.

This construction of passage 20 allows a gas and powder jet of a predetermined profile to be formed, ensures efficient acceleration of the powder, and lowers velocity decrease in the compressed gas layer in front of the surface being coated.

A swirl member 21 for swirling the gas flow admitted to nozzle 13 through pipe 8 and leaving the means for compressed gas supply is provided on the inner surface of intermediate nozzle 13, at the outlet thereof in mixing chamber 3. This swirl member 21 ensures an effective removal of powder and formation of a gas and powder mixture. To provide a recoil flow and ensure an effective mixing of powder and gas when the gas flow runs into the portion of cylindrical periphery 9' of drum 9 forming wall 17 of mixing chamber 3, intermediate nozzle 13 is mounted in such a manner that its longitudinal axis O-O extends at an angle from 80 to 85° with respect to a normal "n-n" drawn to cylindrical periphery 9' of drum 9.

The apparatus for applying a coating to the surface of a product also comprises a means for supplying compressed gas to depressions 10 in cylindrical periphery 9' of drum 9 and to a top part 22 of hopper 2 so as to even out pressure in hopper 2 and in mixing chamber 3. This facility allows the effect of pressure on metering of the powder to be eliminated.

The means for gas supply is in the form of a passage 23 in casing 1' of metering feeder 1 which connects an interior space 24 of intermediate nozzle 13 to top part 22 of hopper 2 and has a tube 25 which is connected to intermediate nozzle 13, extends through hopper 2 and is bent, at its top part, at 180°.

The means constructed as described above ensures reliable operation and prevents powder from getting into passage 23 when the powder is loaded into hopper 2.

To facilitate control of gas escape velocity by varying its temperature, hence, velocity of powder particles, another embodiment of the apparatus has a means 27 (Fig. 4) for heating compressed gas and a gas temperature control system which allow gas and powder mixture velocity to be controlled when it moves through nozzle 4 for acceleration of powder particles.

The gas temperature control system has a power supply 28 which is electrically coupled, via terminals 29, by means of cables 30, to a gas heating means, a temperature indicator 31, and a thermocouple 32 engageable with the body of nozzle 4.

Gas heating means 27 is connected in series with metering feeder 1.

To enhance heat transfer from the heater to gas, an inlet 33 of means 27 for heating compressed gas is connected, by means of a pneumatic line 34, to mixing chamber 3 of metering feeder 1, and its outlet 35 is connected, by means of a pneumatic line 36, to nozzle 4 for acceleration of powder particles.

If a coating is applied with polymeric materials, the apparatus is provided with a forechamber 37 (Fig. 5) mounted at the inlet of nozzle 4 for acceleration of powder particles. Inlet 33 of means 27 for heating compressed gas and an inlet 38 of metering feeder 1 are connected by means of individual pneumatic lines 39 to compressed gas supply 5, and their outlets 35 and 40 are connected, by means of other pneumatic lines 41, to forechamber 37. This embodiment of the apparatus has the parallel connection of means 27 for gas heating to metering feeder 1. Means 27 for compressed gas heating has a casing 42 (Fig. 4) which has an inner heat insulator 43. Casing 42 accommodates a heating element 44 made of a resistor alloy in the form of a spiral of a thin-walled tube in which the gas flows.

To reduce the effect of the gas supplied from metering feeder 1 on operation of supersonic nozzle 4, forechamber 37 has a diaphragm 45 (Fig. 5) mounted therein and having ports 46 for evening out gas velocity over the cross-section, and a pipe 47 mounted in forechamber 37 coaxially with diaphragm 45 for introducing powder particles from metering feeder 1. The cross-sectional area of pipe 47 is substantially 5 to 15 times as small as the cross-sectional area of pneumatic line 41 connecting means 27 for gas heating to forechamber 37.

Drum 9 is mounted for rotation in a sleeve 48 (Fig. 6) made of a plastic material which engages cylindrical periphery 9' of drum 9.

The plastic material of sleeve 40 is a fluoroplastic (teflon) which ensures the preservation of shape of drum 9 by absorbing powder particles.

The provision of sleeve 48 lowers wear of drum 9 and reduces alterations of its surface 9', and jamming is eliminated.

5 The apparatus for applying a coating shown in Fig. 1 functions in the following manner. A compressed gas from gas supply 5 is supplied along pneumatic line 6, via shut-off and control member 7, to inlet pipe 8 of metering feeder 1, the gas being accelerated by means of intermediate nozzle 13 and directed at an angle of between 80 and 85° to impinge against cylindrical periphery 9' of drum 9 which is stationary and then gets into mixing chamber 3 from which it escapes through profiled supersonic nozzle 4. Supersonic  
10 nozzle 4 is adjusted to have a working mode (5 to 20 atm.) by acting upon shut-off and control member 7 so as to form a supersonic gas jet at a velocity ranging from 300 to 1200 m/s.

Powder from hopper 2 gets to cylindrical periphery 9' of drum 9 to fill depressions 10 and, during rotation of the drum, the powder is transferred into mixing chamber 3. The gas flow formed by intermediate nozzle 13 and turbulized by swirl member 21 blows the powder off cylindrical periphery 9' of drum 9 into  
15 mixing chamber 3 wherein a gas and powder mixture is formed. Flow rate of the powder in an amount between 0.05 and 17 g/s cm<sup>2</sup> is set up by the rotary speed of drum 9 and powder flow controller 11. Deflector 15 prevents the powder from getting into space 14 between casing 1' and drum 9. The gas from intermediate nozzle 13 is also taken in along passages 23 and gets into space 12 between drum 9 and casing 1' so as to purge it and clean it from residues of the powder, and gas gets, through tube 25, into top  
20 part 22 of hopper 2 so as to even out pressure in hopper 2 and mixing chamber 3. A gas and powder mixture from mixing chamber 3 is accelerated in supersonic portion 20 of passage 18. A high-speed gas and powder jet is thus formed which is determined by the cross-sectional configuration of passage 18 with the velocity of particles and density of their flow rate necessary for the formation of a coating. For a given profile of supersonic portion 20 of passage 18, the density of flow rate of powder particles is set up by  
25 metering feeder 1, and the velocity is determined by the gas used. For example, by varying percentage of helium in a mixture with air between 0% and 100%, the velocity of powder particles can be varied between 300 and 1200 m/s.

The apparatus for applying a coating shown in Fig. 4 functions in the following manner.

A compressed gas from gas supply 5 is fed, via pneumatic line 6 and shut-off and control member 7  
30 which adjusts pressure between 5 and 20 atm. in the apparatus, to metering feeder 1 having its drum 9 which is stationary. The gas then flows through metering feeder 1 and is admitted, via pneumatic line 34, to heating element 44 of gas heating means 27 in which the gas is heated to a temperature between 30 and 400°C, which is determined by the gas temperature control system. The heated gas is supplied through pneumatic line 36 to profiled supersonic nozzle 4 and escapes therefrom owing to gas expansion. When the  
35 apparatus is in the predetermined mode of jet escape, drum 9 of metering feeder 1 is rotated, and the desired concentration of powder particles is adjusted by means of powder flow controller and by varying speed of drum 9, and the velocity of the powder particles accelerated by supersonic nozzle 4 is set up by varying the gas heating temperature.

In depositing polymeric powders, an apparatus is used (Fig. 5) in which powder from metering feeder 1  
40 is fed directly through pipe 41 to mixing forechamber 37, and in which the gas heated in heating means 27 passes through ports 46 of diaphragm 45 to transfer the powder into supersonic nozzle 4 in which the necessary velocity is imparted to the particles.

#### Embodiments of the Invention

##### 45 Example 1

The apparatus shown in Fig. 1 was used for coating application.

Working gas was air. Air pressure was 9 atm., flow rate was 0.05 kg/s, deceleration temperature was  
50 7°C. Mach number at the nozzle edge was 2.5 to 4. The product material was steel and brass.

Aluminium powder particle size was from 1 to 25 µm, a density of flow rate of the powder was between 0.01 and 0.3 g/s cm<sup>2</sup>, a velocity of particles ranged from 300 to 600 m/s.

Coating conditions are given in Table 1.

Table 1

No.	Flow rate density, g/s cm <sup>2</sup>	Treatment time,	Coating thickness, m	Change in temperature of heat-insulated support, °C
1	0.01	1000	-	2
2	0.05	20	8	6
3	0.05	100	40	6
4	0.10	100	90	14
5	0.15	100	150	20
6	0.3	100	390	45

It can be seen from the Table that the coating is formed with a flow rate density of powder from 0.05 g/s cm<sup>2</sup> and up. With an increase in density of powder flow rate up to 0.3 g/s cm<sup>2</sup>, temperature of the heat insulated support increases up to 45 °C.

It follows from the above that coatings can be applied under the above-mentioned conditions, and products have a minimum exposure to thermal effects.

Examples 2, 3, 4, 5 and 6.

The apparatus shown in Fig. 1 was used for coating application.

The material of deposited powders was copper, aluminium, nickel, vanadium, an alloy of 50% of copper, 40% of aluminium, and 10% of iron.

The support material was steel, duralumin, brass, and bronze, ceramics, glass: the support was used without heat insulation.

Operation conditions of the apparatus:

gas pressure 15 to 20 atm.;

gas deceleration temperature 0 to 10 °C;

Mach number at the nozzle edge 2.5 to 3;

working gas- mixture of air and helium with 50% of helium;

gas flow 20 to 30 g/s;

particle flow rate density 0.05 to 17 g/s cm<sup>2</sup>.

The velocity of particles was determined by the method of laser Doppler anemometry, and the coefficient of utilization of particles was determined by the weighting method.

The results are given in Table 2

Table 2

Example No.	Particle material	Particle size, $\mu\text{m}$	Particle velocity, m/s	Coefficient of particle utilization, %
1	2	3	4	5
2	copper	1-40	650 $\pm$ 10 800 $\pm$ 10 900 $\pm$ 10 1000 $\pm$ 10	10 30 40 80
3	aluminium	1-25	650 $\pm$ 10 1000 $\pm$ 10 1200 $\pm$ 10	40 60-70 80-90
4	nickel	1-40	800 $\pm$ 10 900 $\pm$ 10 1000 $\pm$ 10	10 40 80
5	vanadium	1-40	800 $\pm$ 10 900 $\pm$ 10 1000 $\pm$ 10	10 30 60
6	alloy	10-100	700 $\pm$ 10 800 $\pm$ 10 900 $\pm$ 10	10 20 50

It can be seen from Table 2 that with an increase in velocity of particles for all materials, the coefficient of utilization increases, but its values differ for different materials. The support temperature in all cases did not exceed 50 to 70 °C.

After a prolonged operation with application of coatings, with the time of operation of the apparatus of at least 100 hours, various components of the apparatus have been inspected and it has been revealed that the nozzle profile did not have any alterations, and thin films coated the nozzle in the zone of its critical section and in the supersonic portion thereof as a result of friction with the nozzle walls during movement. These films did not have any effect on operating conditions of the nozzle. Individual inclusions of particles being deposited have been found in the fluoroplastic sleeve of the metering feeder, but the configuration of the drum and depressions of its cylindrical periphery remained substantially unchanged.

Therefore, service life of reliable operation of the apparatus amounted to at least 1000 hours. The absence of energy-stressed components makes the upper limit of the throughput capacity substantially unlimited.

#### Example 7

The apparatus shown in Fig. 4 used for application of coatings had the following parameters:

Mach number at the edge of the nozzle	2.5 to 2.6
gas pressure	10 to 20 atm;
gas temperature	30 to 400 °C;
working gas	air;
gas flow	20 to 30 g/s;
powder flow	0.1 to 10 g/s;
powder particle size	1 to 50 $\mu\text{m}$ .

The coatings were applied with particles of aluminium, zinc, tin, copper, nickel, titanium, iron, vanadium, cobalt to metal products, and the coefficient of utilization of the powder was measured (in percent) versus air heating temperature and related velocity of powder particles.

The results are given in Table 3

Table 3

Powder material	Air temperature, °C					
	10	30	100	200	350	400
aluminium	0.1-1%	1-1.5	10	30-60	90-95	
zinc	1-2	2-4	10	50-80		
tin	1-30	80-40	40-60			
copper			10-20	50	80-90	90
nickel				20	50-80	80-90
titanium				50-80	-	-
iron				20-40	60-70	80-90
vanadium		-		20	40-50	60-70
cobalt				20	40-50	50-60

It can be seen from Table 3 that when air is used as working gas at room temperature, high-quality coatings can be produced from powders of such plastic metals as aluminium, zinc, and tin. A slight air heating to 100-200 °C resulting in an increase in particle velocity allows coatings to be produced from the majority of the above-mentioned metals. The product temperature does not exceed 60 to 100 °C.

#### Example 8

The apparatus shown in Fig. 5 was used for coating application.

Mach number at the edge of the nozzle	1.5 to 2.6;
gas pressure	5 to 10 atm;
gas temperature	30 to 180 °C;
working gas	air;
gas flow	18 to 20 g/s;
powder flow	0.1 to 1 g/s;
powder particle size	20 to 60 µm.

A polymer powder was applied to products of metal, ceramics, and wood. A coating thickness was from 100 to 200 µm. Further thermal treatment was required for complete polymerization.

It can be seen from the above that the invention makes it possible to;

- apply coatings from several dozens of microns to several millimeters thick of metals, their mechanical mixtures, alloys, and insulating materials to products of metals, alloys, and insulating materials, in particular, to ceramics and glass with a low level of thermal exposure of the products;
- apply coatings with fine powders, with particle size between 1 and 10 µm without phase transformations, appearance of oversaturated structures, and hardening during coating formation;
- enhance efficiency of acceleration of the powder owing to the use of compressed high-density gases;
- substantially lower thermal exposure of components of the apparatus.

The construction of the apparatus ensures its operation during at least 100 hours without the employment of expensive erosion-resistant and refractory materials, high throughput capacity which is substantially unlimited because of the absence of thermally stressed components so that this apparatus can be incorporated in standard flow lines to which it can be readily matched as regards the throughput capacity, e.g., in a flow line for the manufacture of steel pipes having protective zinc coatings.

#### Industrial Applicability

The invention can be most advantageously used, from manufacturing and economic point of view in restoring geometrical dimensions of worn parts increasing wear-resistance, protecting of ferrous metals against corrosion.

The invention may be advantageously used in metallurgy, mechanical engineering, aviation and agricultural engineering, in the automobile industry, in the instrumentation engineering and electronic technology for the application of corrosion-resistant, electrically conducting, antifriction, surface-hardening,

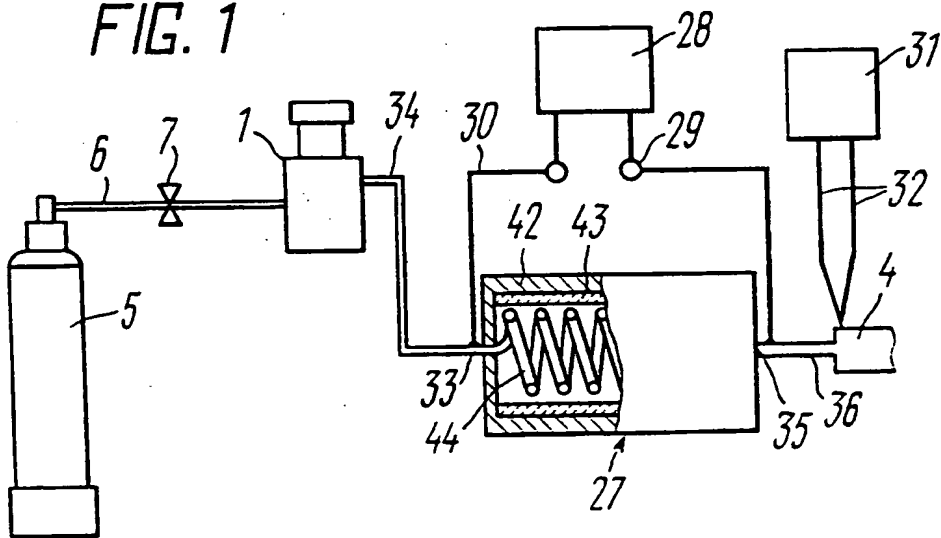
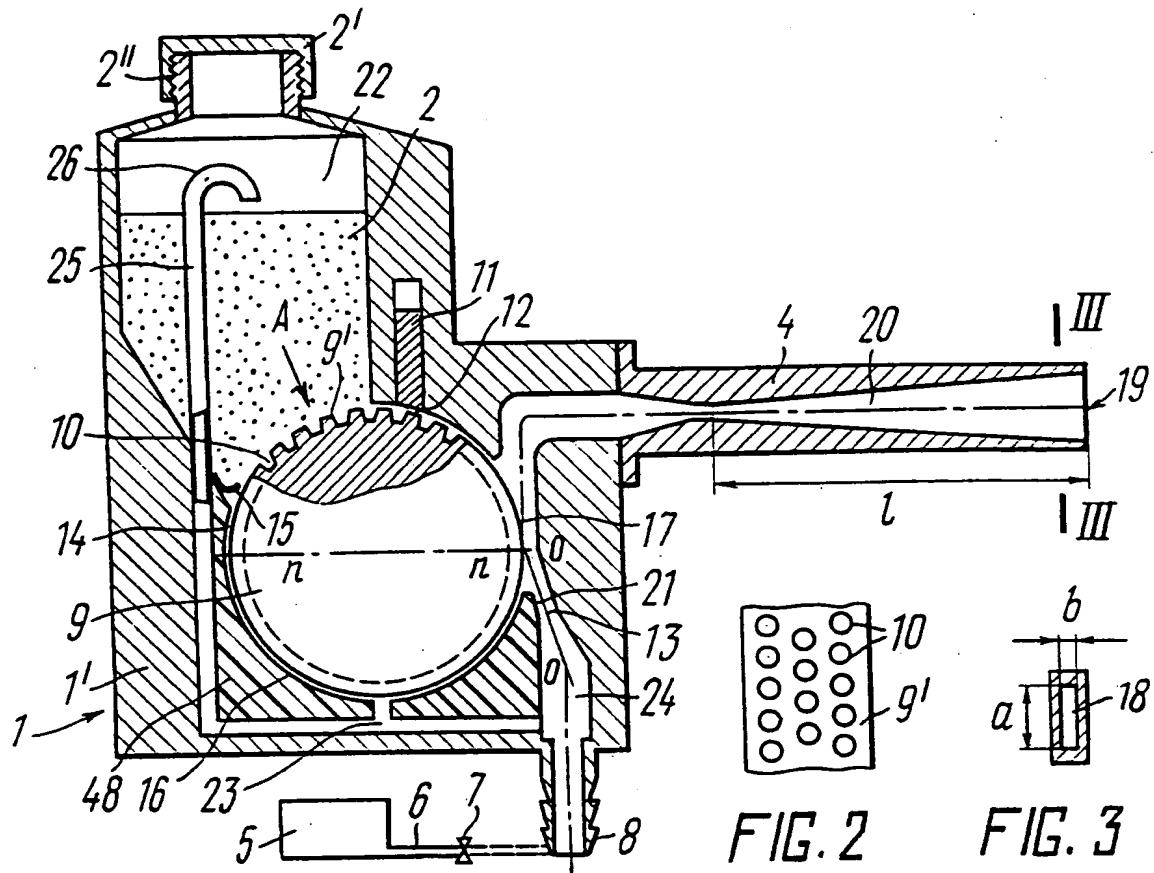
magnetically conducting, and insulating coatings to parts, structures, and equipment which are manufactured, in particular, of materials capable of withstanding a limited thermal load and also to large-size objects such as sea-going and river vessels, bridges, and large-diameter pipes.

The invention may also find application for producing multiple-layer coatings and combined (metal-polymer) coatings as part of comprehensive manufacturing processes for producing materials with expected properties.

#### Claims

1. A method for applying coatings to the surface of a product made of a material selected from the group consisting of metals, alloys, and insulating materials, comprising introducing into a gas flow a powder of a material selected from the group consisting of metals, alloys, their mechanical mixtures or insulating materials for forming a gas and powder mixture which is directed towards the surface of a product, **characterized** in that the powder used has a particle size from 1 to 50  $\mu\text{m}$  in an amount ensuring flow rate density of the particles between about 0.05 and about 17 g/s  $\text{cm}^2$ , a supersonic velocity being imparted to the gas flow, and a supersonic jet of a predetermined profile being formed which ensures a velocity of powder in the gas and powder mixture from 300 to 1200 m/s.
2. A method according to claim 1, **characterized** in that the formation of a supersonic jet of a predetermined profile is carried out by expanding gas according to a linear law.
3. A method according to claim 1, **characterized** in that the gas is used which is under a pressure of from about 5 to about 20 atm. and at a temperature below the melting point of the powder particles.
4. A method according to claim 1, **characterized** in that the gas for a gas flow is air.
5. A method according to claim 1, **characterized** in that the gas for a gas flow is helium.
6. A method according to claim 1, **characterized** in that the gas for a gas flow is a mixture of air and helium.
7. A method according to claim 1, **characterized** in that the gas for a gas flow is heated to a temperature from about 30 to about 400 °C.
8. An apparatus for carrying out the method of claim 1, comprising a metering feeder (1) having a casing (1') incorporating a hopper (2) for a powder communicating with a means for metering the powder in the form of a drum (9) having depressions (10) in its cylindrical periphery (9'), and a mixing chamber (3) communicating therewith, and a nozzle (4) for accelerating powder particles communicating with the mixing chamber (3), a compressed gas supply (5), and a means connected thereto for supplying compressed gas to the mixing chamber (3), **characterized** in that it comprises a powder particle flow controller (11) which is mounted in a spaced relation (12) to the cylindrical periphery (9') of the drum (9), with a space ensuring the necessary flow rate of the powder, and an intermediate nozzle (13) coupled to the mixing chamber (3) and communicating, via an inlet pipe (8) thereof, with the means for supplying compressed gas, the metering feeder (1) having a deflector (15) mounted on the bottom of the hopper (2) adjacent to the cylindrical periphery (9') of the drum (9) which has its depressions (10) extending along a helical line, the drum (9) being mounted horizontally in such a manner that one portion of its cylindrical periphery (9') defines the bottom of the hopper (2) and the other portion thereof defines the wall (17) of the mixing chamber (3), the particle acceleration nozzle (4) being in the form of a supersonic nozzle and having a profiled passage (18).
9. An apparatus according to claim 8, **characterized** in that the passage (18) of the nozzle (4) for acceleration of particles has one dimension (a) of its cross-section larger than the other (b), with the ratio of the smaller dimension (b) of the cross-section at the edge (19) of the nozzle (4) to the length (l) of the supersonic portion (20) of the passage (18) ranging from about 0.04 to about 0.01.
10. An apparatus according to claim 8, **characterized** in that a swirl member (21) for swirling the gas flow leaving the means for compressed gas supply is provided on the inner surface of the intermediate nozzle (13), at the outlet thereof in the mixing chamber (3).

11. An apparatus according to claim 8, **characterized** in that the intermediate nozzle (13) is mounted in such a manner that its longitudinal axis (0-0) extends at an angle from 80 to 85° with respect to the normal (n-n) to the cylindrical surface (9') of the drum (9).
- 5 12. An apparatus according to claim 8, **characterized** in that the apparatus comprises a means for supplying compressed gas to depressions (10) in the cylindrical periphery (9') of the drum (9) and to the upper part (22) of the hopper (2) so as to even out pressure in the hopper (2) and mixing chamber (3).
- 10 13. An apparatus according to claim 12, **characterized** in that the means for gas supply is made in the casing (1') of the metering feeder (1) in the form of a passage (23) connecting the interior space (24) of the intermediate nozzle (13) to the interior space (22) of the hopper (2) and also comprises a tube (25) connected to the intermediate nozzle (13) and extending through the hopper (2), the top part (26) of the tube being bent at 180°.
- 15 14. An apparatus according to claim 8, **characterized** in that the apparatus comprises a means (27) for heating compressed gas having a gas temperature control system for controlling velocity of gas and powder mixture in the nozzle (4) for powder particle acceleration.
- 20 15. An apparatus according to claim 14, **characterized** in that the inlet (33) of the means (27) for gas heating is connected, through a pneumatic line (34) to the mixing chamber (3) of the metering feeder (1) and the outlet (35) is connected to the nozzle (4) for acceleration of powder particles.
- 25 16. An apparatus according to claim 14, **characterized** in that it comprises a forechamber (37) mounted in the inlet of the nozzle (4) for acceleration of powder particles, the inlets (33, 38) of the means (27) for gas heating and of the inlet pipe of the intermediate nozzle (13) of the metering feeder (1) being connected, by means of individual pneumatic lines (39) to a compressed gas supply (5) and their outlets (35, 40) being connected to the forechamber (37) by means of other individual pneumatic lines (41).
- 30 17. An apparatus according to claim 14, **characterized** in that the heating means (27) is provided with a heating element (44) made of a resistor alloy.
- 35 18. An apparatus according to claim 17, **characterized** in that the heating element (44) is mounted in a casing (42) having a heat insulation (43) inside thereof.
- 40 19. An apparatus according to claim 17, **characterized** in that the heating element (44) is made in the form of a spiral of a thin-walled tube, with the gas flowing through the tube.
- 45 20. An apparatus according to claim 17, **characterized** in that the forechamber (37) has a diaphragm (45) mounted in its casing and having ports (46) for evening out the gas flow over the cross-section and a pipe (47) coaxially mounted in the diaphragm for introducing powder particles, the cross-sectional area of the pipe being substantially 5 to 15 times as small as the cross-sectional area of the pneumatic line (41) connecting the gas heating means (27) to the forechamber (37).
- 50 21. An apparatus according to claim 8, **characterized** in that the drum (9) is mounted for rotation in a sleeve (48) made of a plastic material which engages the cylindrical periphery (9') of the drum (9).
- 55 22. An apparatus according to claim 21, **characterized** in that the plastic material of the sleeve (48) is fluoroplastic (teflon).



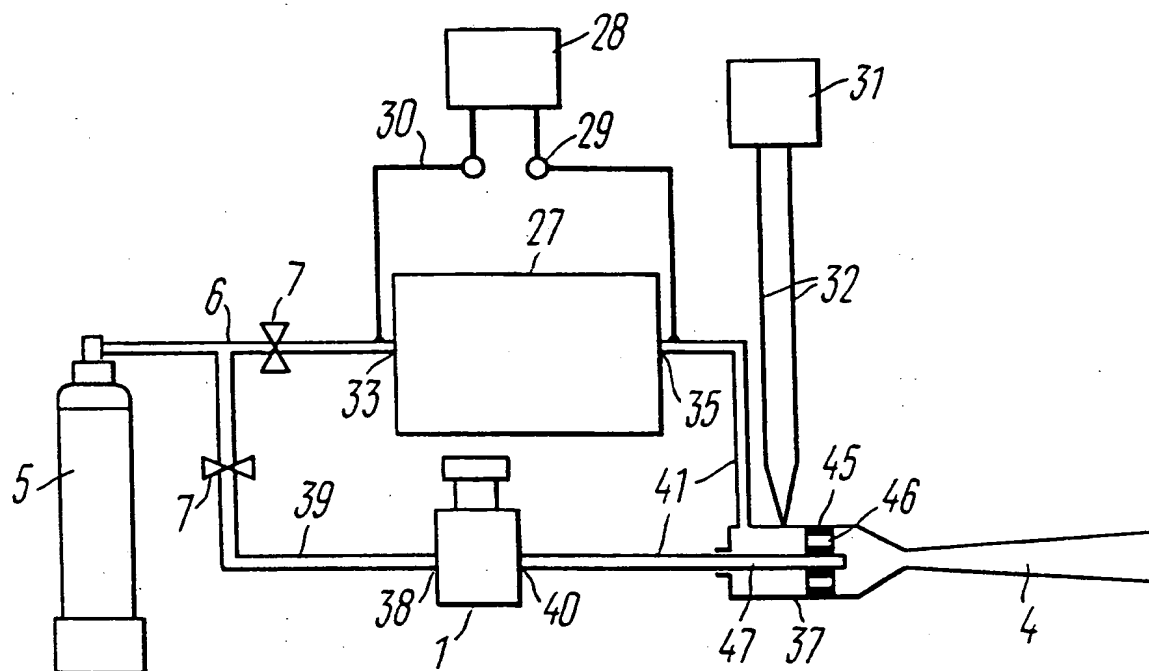


FIG. 5

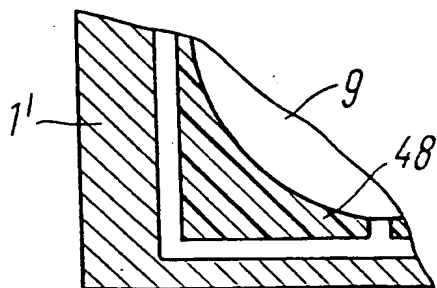


FIG. 6

# INTERNATIONAL SEARCH REPORT

International Application No PCT/SU 90/00126

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>5</sup> C23C 4/00, B05B 7/24, B05C 19/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC <sup>5</sup> C	C23C 4/00, 4/12, B05B 7/14, 7/24, B05C 19/00	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b>		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
A	EP, A1, 0261973 (CANON KABUSHIKI KAISHA) 30 March 1988 (30.03.88) the abstract	8,9,14,15, 17-19
A	US, A, 4815414 (NYLOK FASTENER CORPORATION) 28 March 1989 (28.03.89) the abstract	8,10,12
A	WO, A1, 88/04202(NORDSON CORPORATION) 16 June 1988 (16.06.88) the abstract	8-11,16,20 21
A	Khasui A. "Tekhnika napylenia", 1975 Mashinostroenie (Moscow) pages 16,18	1-3,7
A	Usov L.N. et al.: "Primenenie plazmy dlya poluchenia vysokotemperaturnykh pokryty", 1965, Nauka (Moscow), pages 17,18,59-61	1,4-7
A	Krnyk R. "Metallizatsia raspyleniem", 1956, Profizdat, page 86	3
-----		
<p>* Special categories of cited documents: **</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
22 March 1991 (22.03.91)		08 April 1991 (08.04.91)
International Searching Authority		Signature of Authorized Officer
ISA/SU		